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THE ANOMALOUS METALLOPORPHYRIN AND CHLOROPHYLL A ACTIVATED CHEM--ETC(U)
FEB 80 S P SCHMIDT, G B SCHUSTER N00014-76-C-0745
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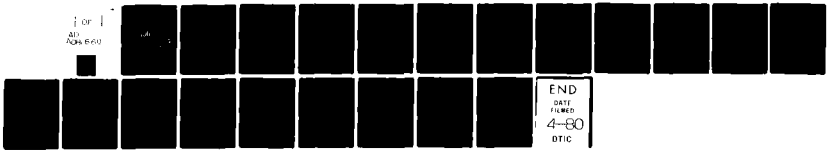

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A wide range of fluorescent electron donors catalyze the chemiluminescence of dimethyldioxetanone (1) by the chemically initiated electron-exchange luminescence (CIEEL) pathway. In general, the magnitude of the catalytic rate constant, the efficacy of excited state generation correlate well with the one electron oxidation potential of the donor. Exceptions to this correlation are several zinc and magnesium porphyrins, including chlorophyll a, for which their chemiluminescent catalysis is much greater than predicted by their oxidation potentials. The critical (cont.)

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role of the central metal atom in eliciting this unusual behavior was evaluated by determining the catalytic rate constants and the initial chemiluminescence intensity of several non-metallated as well as differently metallated porphyrins. These results suggest that formation of a ground state complex between 1 and certain metalloporphyrins is the cause of the unusual catalysis. Spectroscopic evidence of a ground state complex between zinc tetraphenyl porphyrin (ZnTPP) and tetramethyldioxetane, a model for 1, has been obtained.

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TECHNICAL REPORT NO. N0014-76-C-0745-24

# The Anomalous Metalloporphyrin and Chlorophyll a Activated Chemiluminescence of Dimethyldioxetanone. Chemically Initiated Electron-Exchange Luminescence.

by

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Feb[redacted]

The chemistry of the dioxetane ring system has been under active investigation for the past decade.[2] In a recent report[3] we described our discovery of the operation of the chemically initiated electron-exchange luminescence (CIEEL) mechanism[4] in the chemiluminescence of dimethyldioxetanone (1). The involvement of this mechanism was indicated primarily by the correlation of the excited state generating effectiveness of a wide range of electron donors with the one electron oxidation potential ($E_{ox}$) of the donor. In that report we noted that zinc tetraphenylporphyrin (ZnTPP) is an apparent exception to this correlation. The initial chemiluminescent light intensity from ZnTPP is about 100 times greater than is predicted simply from its one electron oxidation potential. Moreover, the observed rate constant for catalysis of the decomposition of 1 by ZnTPP is much larger than is predicted by its oxidation potential.

Unusual chemiluminescent phenomena have been reported previously for metalloporphyrins. Linschitz observed emission from the thermolysis of decalin hydroperoxide in the presence of ZnTPP or chlorophyll.[5] He noted that the free-base porphyrin, unlike ZnTPP, has no catalytic effect on the rate of reaction of decalin hydroperoxide. Moreover, the free-base reaction is not chemiluminescent. More recently, McCapra reported chemiluminescence from the reaction of a variety of peroxides with ZnTPP.[6] Again the metal is an absolute requirement.

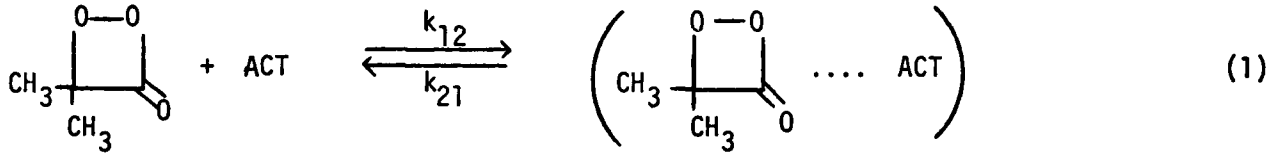
In this report we describe our investigation of the interaction of ZnTPP and other metallo- and free-base prophyrins with dioxetanone 1. The results of this investigation show conclusively for the first time that the unusual behavior of ZnTPP is consistent with the CIEEL mechanism and that this behavior is due to the formation of a ground state complex between the peroxide and the metalloporphyrin.

## Results and Discussion

In our previous report we established that the mechanism for electron donor (activator, ACT) catalyzed chemiluminescence of dioxetanone 1 proceeds by

a rate limiting electron transfer from ACT to the peroxide generating eventually acetone radical anion and ACT radical cation. Annihilation of these oppositely charged radical ions forms the excited state of ACT which we detect by it characteristic luminescence. This mechanism, and the appropriate rate constants, are shown in Scheme 1.

Scheme 1

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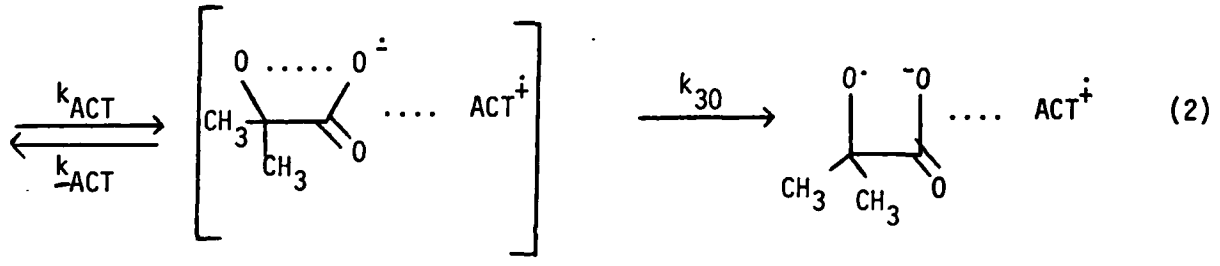


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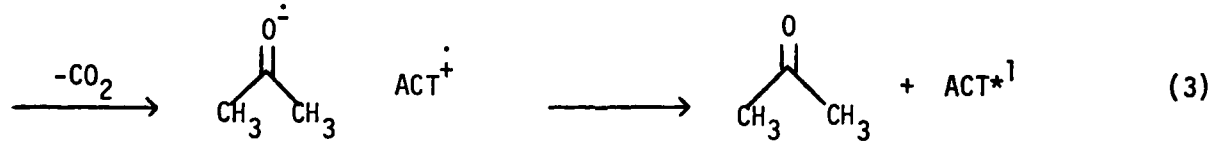



(3)

Our results indicate that the kinetics of the activator catalyzed reaction conform to:

$$k_{obs} = k_1 + k_{cat}\,[ACT] \qquad (4)$$

where $k_{obs}$ is the rate constant for the observed net first order consumption of dioxetanone 1, $k_1$ is the rate constant for reaction of 1 in the absence of ACT, and $k_{cat}$ is rate constant for the bimolecular reaction of 1 and ACT. It is the bimolecular interaction that is primarily responsible for the chemiluminescence.

The ratio of initial chemiluminescence intensity ($I_o$) to the fluorescence efficiency of ACT ($\phi_f$) can be related to the magnitude of $k_{cat}$, and the initial concentrations of 1 and ACT according to:

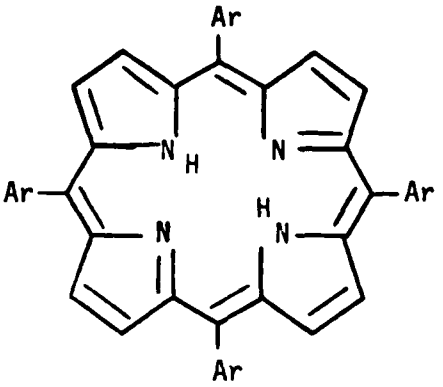
$$I_o/\phi_f = k_{cat}\,[1]_o[ACT] \qquad (5)$$

Thus under conditions where the concentrations of 1 and ACT are constant during the time required for the experiment, $I_o/\phi_f$ is directly proportional to $k_{cat}$. We have measured $I_o/\phi_f$ under these conditions for a wide variety of ACT. In general, for amine and aromatic hydrocarbon ACT their $E_{ox}$ accurately predict the magnitude of $I_o/\phi_f$. The exceptions to this correlation are some metalloporphyrins, Figure 1. The measured value of $k_{cat}$ for a variety of ACT are presented in Table I. It should be noted that the exceptionally large value of $I_o/\phi_f$ for the zinc and magnesium porphyrins are consistent with the independently measured values for $k_{cat}$.

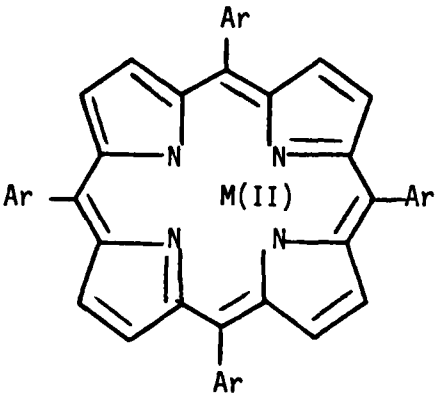
In order to determine if the unusual catalytic ability of the zinc and magnesium porphyrins is due to the metal ion or to the porphyrin ring system we investigated the behavior of some free-base porphyrins. In particular, we determined $I_o/\phi_f$ and $k_{cat}$ for tetraanisylporphyrin ($H_2TAP$). As can be seen from Figure 1 and Table I, $H_2TAP$ does not behave unusually. That, is its $E_{ox}$ is a reliable predictor of both $I_o/\phi_f$ and $k_{cat}$. Similarly, tetraphenylporphyrin ($H_2TPP$) does not appear to catalyze the decomposition of 1 or its chemiluminescence beyond that which would be predicted by its $E_{ox}$. Evidently, the metal ion plays a crucial role in causing the unusually efficient catalysis by MgTPP and ZnTPP.

To probe further the mechanism of this metal ion catalysis we examined the effect of changing the metal ion on $I_o/\phi_f$ and $k_{cat}$ for tetraphenyl- and tetraanisyloporphyrins. Cyclic voltammetric measurements have revealed that for

zinc, cadmium, and magnesium porphyrins the first oxidation is ligand centered.[7] On the other hand, for silver and cobalt porphyrin the first oxidation is metal centered.[7,8] Interestingly, zinc, cadmium, cobalt, and magnesium porphyrin (including chlorophyll a) exhibit the unusually effective catalysis, but AgTPP does not. The magnitude of $k_{cat}$ for AgTPP is accurately predicted by its $E_{ox}$, Table I. Evidently, the identity of the metal ion matters greatly for the catalysis. Compare, for example, AgTPP ($E_{ox}$ = 0.59 V vs SCE) which exhibits a $k_{cat}$ of 1.1 $M^{-1}$ $s^{-1}$ and MgTPP ($E_{ox}$ = 0.60 V vs SCE) whose $k_{cat}$ is nearly 10,000




Free-Base Porphyrins
$H_2$TPP, Ar=Ph
$H_2$TAP, Ar=(p-$OCH_3$)Ph




Metalloporphyrins
MTPP, Ar=Ph
MTAP, Ar=(p-$OCH_3$)Ph

times larger. But, the catalysis can occur with metalloporphyrins that undergo either metal- or ligand-centered oxidation. Apparently, it is some feature other than the site of oxidation of the metalloporphyrin that engenders the remarkable chemiluminescent catalysis.

It is quite well known that certain metalloporphyrins form stable complexes with nitrogen bases such as pyridine.[9] Moreover, it is known that free-base porphyrins do not form these complexes.[10] Quite recently the results of a thermodynamic study of the complex formation of ZnTPP with several neutral donors was reported.[11] In this study the equilibrium constant for the complex was

estimated by the shift of the maximum of the porphyrin Soret absorption band. For metalloporphyrins it has been observed that the maximum of the Soret band shifts to longer wavelengths upon complex formation. For simple ester donors the shift in cyclohexane solution is observed to be ca. 5 nm, for alkyl ethers ca. 6 nm. We investigated the possibility that the formation of a ground state complex between dioxetanone 1 and certain metalloporphyrins is the cause of the unusual catalysis.

Addition of ZnTPP or MgTPP to cyclohexane solutions of dioxetanone 1 causes such a rapid reaction that it is not possible for us to measure the absorption spectrum of the mixture before most of the peroxide has reacted. To circumvent this problem we used tetramethyldioxetane (2) as a model for 1. The reactions of 2 are not particularly sensitive to metalloporphyrin catalysis, presumably because its reduction potential is far more negative than that of 1. In cyclohexane solution the maximum of the Soret band for ZnTPP is at 416.0 nm. In the presence of 0.36 M 2 this maximum shifts to 417.2 nm. A similar result is obtained with MgTPP. Interestingly, AgTPP, which does not readily expand its coordination sphere,[12] and for which no special catalysis is observed, does not give evidence of complex formation with dioxetane 2. This is in line with our observation that even pyridine does not shift the absorption maximum or oxidation potential of this metalloporphyrin. Evidently the ability of the metalloporphyrin to form detectable complexes with dioxetane 2 predicts reliably the unusual catalytic behavior.

The magnitude of $k_{cat}$ is related to several of the rate constants specified in Scheme 1. Our previously reported data indicates that $k_{30} >> k_{-ACT}$. Thus simple analysis of the kinetics show that:

$$k_{cat} = K_{12}\, k_{ACT} \qquad (6)$$

where $K_{12}$ ($k_{12}/k_{21}$) is the equilibrium constant for complex formation.[13] For the amine and aromatic hydrocarbon activators $K_{12}$ is evidently independent of the structure of ACT and probably depends, as in the Weller model,[14] only on diffusion. However, ZnTPP, MgTPP, CoTPP, CdTPP, etc. form ground state complexes with peroxide 1 and the magnitude of $k_{cat}$ is therefore the product of $K_{12}$ for the complex and $k_{ACT}$. Indeed, if we assume that complexation does not affect $k_{ACT}$ then we can estimate the magnitude of $K_{12}$ from the measured value of $k_{cat}$ and an interpolated (from the $E_{ox}$ vs. $I_o/\phi_f$ plot) value for $k_{ACT}$. The $K_{12}$ of ZnTPP, is thereby estimated to be 100 $M^{-1}$, a value consistent with equilibrium constants reported by others for complexes of metalloporphyrins with various oxygen donors.[11]

The electron transfer reaction of chlorophyll a (Chla) continue to be of general interest due to their intimate involvement in the initiating steps of photosynthesis. In connection with their study of the electrochemistry of Chla, Saji and Bard reported their observation of electrogenerated chemiluminescence of Chla in the presence of oxygen.[15] In our system Chla behaves much like the synthetic magnesium and zinc porphyrins in eliciting efficient chemiluminescence from 1 by the electron-exchange pathway. The magnitude of the Chla catalytic rate constant is comparable to that of the magnesium tetraphenylporphyrins (Table I), suggesting that ground state complex formation with peroxide 1 is important for Chla as well. It is likely therefore that other Chla - Peroxide systems might also be chemiluminescent, the result of an analogous complexation -electron transfer sequence. As noted by others,[15] for example, weak chemiluminescence has been observed from the reaction of $O_2$ with photoreduced chlorophyll.[16]

While the magnesium and zinc porphyrins are among the most effective activators of chemiluminescence for 1 which we have found, they are quite ineffective in catalyzing chemiluminescence with diphenoylperoxide (DPP). This might be surprising initially in light of the established involvement of the CIEEL pathway for the chemiluminescence of DPP in the presence of aromatic hydrocarbons.[4] In

fact, bimolecular rate constants for the catalyzed decomposition of DPP are generally several orders of magnitude larger than for 1 under comparable conditions, a consequence of the more facile reduction of DPP and diacyl peroxides in general than 1 and peroxyesters in general.[3] The metalloporphyrin, however, is consumed in the reaction with DPP. We suspect, therefore, that two electron reduction of DPP is occurring. The second oxidation potentials of these metalloporphyrins are relatively low,[17] in comparison to those of the typical aromatic hydrocarbons which catalyze light formation with DPP. The aroyloxy radical intermediate produced from the one electron reduction and O-O bond cleavage of DPP is more easily reduced than the alkoxy radial derived from the one electron reduction and O-O bond cleavage of 1.[15] Relative rates of decarboxylation may also contribute to the different behavior of 1 and DPP. In any event, further reduction of DPP radical anion effectively removes this species from the light-generating path.

Finally, we would like to point out the remarkable sensitivity of the metalloporphyrin activated chemiluminescence as an analytical technique. The unusually large values of $k_{cat}$ for the complex forming metalloporphyrins, and the emissive properties of ZnTPP and MgTPP conspire to make possible the detection of incredibly small amounts of the metal ions. For example, we have been able to detect unambiguougly ca. 1 ppb zinc in solutions of PdTPP and ZnTPP using dioxetanone 1.

## Conclusion

The chemical reactions of dimethyldioxetanone with a variety of fluorescent electron donors have revealed new features of the CIEEL mechanism. In this report we have described our observation of a ground state complex between this peroxide and several metalloporphyrins. The complex evidently involves an interaction between the metal ion and the peroxide. In all of the cases, and only in those cases, for which complex

formation is detected we observe an increase in both $I_o/\phi_f$ and $k_{cat}$. This finding indicates that the complex is on the reaction path leading to eventual light generation. This remarkably enhanced chemiluminescence catalysis should prove valuable in the detection of trace quantities of these metal ions and in increasing the yield of light when the CIEEL path is in competition with a rapid unimolecular decomposition of the key chemiluminescent intermediate.

## Experimental Section

General. All chemiluminescence measurements were made by the photon counting technique as previously described.[3] Photoexcited fluorescence spectra were obtained on a Farrand Mark V spectrofluorometer, or by photon counting for direct comparison with chemiluminescence emission spectra. UV-VIS absorption spectra were recorded on a Beckman Acta MVI, or Cary 14 instrument. $^1$H NMR spectra were obtained on a Varian HR-220 instrument. Solvents used in the chemiluminescence experiments were purified as previously described.[3]

Cyclic Voltammetry. Cyclic voltammetry was done in argon saturated dichloromethane solution at (23±2)°C with 0.1 M tetra-n-butyl-ammonium perchlorate as supporting electrolyte. A three-electrode system, consisting of platinum working and counter electrodes, and saturated calomel reference electrode (SCE), was used. Scans were made typically at 0.5 V/s. The $E_{ox}$ values were measured as that potential lying midway between the oxidation and reduction peak for a given couple.

Peroxides. Dimethyldioxetanone,[3,18] tetramethyldioxetane,[19] and diphenoylperoxide[4b] were prepared and purified as described elsewhere.

Porphyrins. The porphyrin free bases $H_2$TPP and $H_2$TAP were kindly provided by Prof. Larry Faulkner. They were purified by treatment with dichlorodicyanobenzoquinone (DDQ) in refluxing chloroform, as described by Barnett et al.[20] The porphyrins were shown to be chlorin free by visible absorption spectroscopy.[21]

ZnTPP (Sigma) was also purified by treatment with DDQ.

Other metalloporphyrins were prepared by reaction of the appropriate divalent metal salt with the porphyrin free base in refluxing N,N-dimethylformamide according to the general procedure of Adler et. al.[22] The magnesium porphyrins and CdTPP were recrystallized from benzene-hexane. ZnTAP was purified by dry

column chromatography on $Al_2O_3$, eluting with chloroform, followed by several recrystallizations from chloroform-methanol. CoTPP and AgTPP were purified by dry column chromatography on Florisil, eluting with chloroform, followed by recrystallization from chloroform-methanol.

All porphyrins gave satisfactory elemental analyses, and had visible absorption spectra consistent with literature data.[21,23]

Chlorophyll a (Sigma) was used as received.

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Table I. Oxidation Potentials of Activators and Rate Constants for Their Catalysis of the Reaction of Dioxetanone 1.

| Activator | $E_{ox}$, V[a] | $k_{cat}$, $M^{-1}$ $s^{-1}$[b] |
|---|---|---|
| Chlorophyll a | 0.52[c] | $(1.5\pm0.1)\times10^{3}$ |
| MgTAP | 0.54 | $(2.6\pm0.2)\times10^{4}$ |
| MgTPP | 0.60 | $(1.0\pm0.1)\times10^{4}$ |
| AgTPP | 0.59[d,e] | 1.1±0.2 |
| CdTPP | 0.64[f] | $(2.7\pm0.2)\times10^{3}$ |
| ZnTAP | 0.66[g] | $(1.3\pm0.1)\times10^{3}$ |
| ZnTPP | 0.73 | $(7.0\pm0.2)\times10^{2}$ |
| CoTPP | 0.77[d] | $>10^{5}$[h] |
| $H_2$TAP | 0.80[g] | 0.67±0.03 |
| Rubrene | 0.82 | 0.44±0.02 |

[a] This work, measured in $CH_2Cl_2$, unless otherwise noted. For details see Experimental Section.

[b] Measured in $CH_2Cl_2$ solution at 24.5°C. All errors are standard deviations.

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[d] Metal centered oxidation $M^{II}TPP \rightarrow M^{III}TPP$.

[e] 0.60 V in pyridine.

[f] A. Standienda and G. Biebl, Z. Phys. Chem. (Frankfurt am Main) [N.S.] 52, 254 (1967).

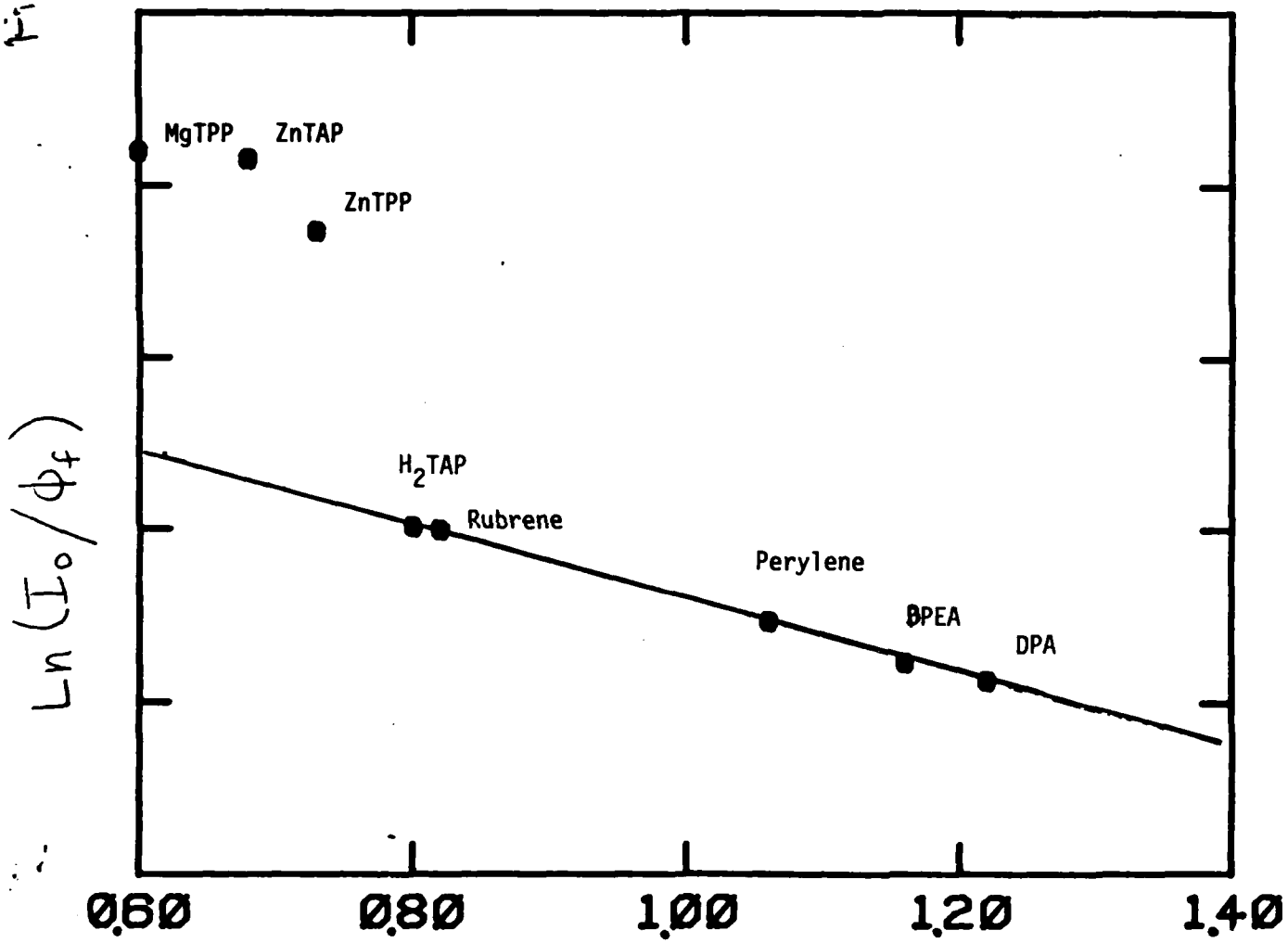
[g] Ref. 7c.

[h] Estimated rate constant.

Caption for Figure

Relationship between the initial chemiluminescence intensity in dichloromethane at 24.5°C, corrected for fluorescence efficiency ($\phi_f$) and photomultiplier tube and monochromator response, and the one electron oxidation potential of the activator: DPA = 9,10-diphenylanthracene, BPEA = 9,10-bis(phenylethynyl) anthracene.

Figure 1


MgTPP
ZnTAP
ZnTPP
$H_2$TAP
Rubrene
Perylene
BPEA
DPA
Ln ($I_o$/$\phi_f$)
0.60
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